168. The Eu(III) Ion as Luminescent Probe: Investigation of the Metal-Ion Sites in a Dicyclohexyl-18-crown-6 Complex[1])

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The metal ion sites of the 3:2 complex between europium nitrate and the A-isomer of dicyclohexyl-18-crown-6, $[Eu(NO_3)_2(DC18C6)]_2[Eu(NO_3)_5]$, have been probed by high-resolution excitation and emission spectra at 296 and 77 K. The $[Eu(NO_3)_5]^{2-}$ anion gives rise to a luminescent spectrum dominated by the $^5D_0 \rightarrow {}^7F_2$ transition. The crystal-field splitting of the ^7F_J levels is close to that observed for $(Phe_4As)_2[Eu(NO_3)_5]$, pointing to a structurally similar pentakis(nitrato) species. The $^5D_0 \leftarrow {}^7F_0$ excitation spectrum of the two crystallographically independent complex cations displays five maxima. A detailed analysis of the corresponding and selectively excited emission spectra leads to the following conclusions. Well differentiated spectra are assigned to different conformations of the complex cation, in which half of the ligand atoms, including O-atoms, present large thermal motions. The other spectra are very similar and arise from slightly unequivalent $[Eu(NO_3)_2(DC18C6)]^+$ moieties differing in the conformation of their ethylene bridges. This demonstrates the sensitivity of the Eu(III) ion as conformational probe in the solid state.

Introduction. – Luminescent lanthanide ions are being extensively used to solve analytical [2] [3] and structural [4] problems. They are especially useful in probing local structures in crystals [5], glasses [6], and solutions [7]. In particular, the Eu(III) ion displays an intense luminescence from a long-lived excited state, $^5D_0$ which, along with its ground-state $^7F_0$, is not split by ligand-field effects. High-resolution, laser-excited excitation and emission spectra of Eu(III)-containing compounds allow the following information to be extracted from a detailed analysis: *i*) the number of chemically different metal-ion sites in the material; *ii*) the total formal charge of the ligating groups directly bound to the Eu(III) ion, and *iii*) the local symmetry of these sites. Moreover, the number of bonded H_2O molecules and the distance between metal ion sites may be estimated from life-time measurements [8]. We have recently shown that indeed the Eu(III) ion behaves as an extremely sensitive probe responding to faint chemical differences, revealing slightly unequivalent moieties present in molecular solids [9]. Such a detailed analysis is not amenable to X-ray or neutron-diffraction studies which yield an averaged image of the unit-cell content, whereas the faster time scale of luminescence experiments provides an instantaneous representation of it.

In continuation of our interest in the relationship between the structure of Eu(III)-containing materials and their luminescent properties [10–12], we report here a photophysical study of the 3:2 complex between europium nitrate and the A-isomer of dicyclo-

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hexyl-18-crown-6 (DC18C6)[3]). According to its crystal and molecular structure [1], this complex is comprised of three independent ions: $[Eu(NO_3)_5]^{2-}$ and two distinct $[Eu(NO_3)_2(DC18C6)]^+$ cations with the ligand in the *cis-syn-cis*-conformation (A-isomer).

Experimental. – The complex was synthesized as described in [1]. Microcrystalline samples were introduced into 1-mm quartz cells *(Interkey 21-Q-6)* fixed onto a specially designed rotable cell-holder to allow for precise alignment. Low-temp. measurements were performed with the help of an *Oxford-DN-704* cryostat controlled by a *DTC-2* variable-temp. unit. Excitation and emission spectra were recorded according to [9]. The dye was *Rhodamine 6G* with an emission band-width of 0.03 nm and an average power of 50–200 mW. Light was conducted to the sample by an *Oriel 77557* liquid optical fiber (100 mm length, 3 mm o.d.). The effective analyzing band-pass was 0.2 nm and 0.05 nm for the conventionally (Xe lamp) and selectively excited spectra, respectively. Wavelength calibration was done with a Hg low-pressure lamp and the accuracy was ≤ 0.1 nm between 575 and 630 nm, and 0.1–0.2 nm over 620 nm. The spectra were digitized by a *Datalab-DL-4000* signal averager (12-bit resolution), transferred into a *Norsk-ND-560* computer and corrected for the response of the spectrometer. Uncertainty on the reported relative intensities is estimated to ±10%.

Lifetimes were measured using a *Lambda-Physik-FL3001* pulsed dye laser *(Rhodamine 6G,* 20-ns pulses, 5–15 mJ/pulse) pumped by a *Lambda-Physik EMG 101-MSC* excimer laser (XeCl, 308 nm, 150 mJ/pulse). Light was conducted to the sample by an *Oriel* liquid optical fiber (200-mm length, 5-mm o.d.). The output signal of the photomultiplier was fed into a *Bruker BC-104* transient recorder (10 MHz, 8-bit resolution) and transferred into the *Norsk-ND-560* computer. The decay curves (300 400 data points over 4–5 lifetimes) were treated both by a multiexponential curve-fitting program (I_{obs} *vs.* time [13]) and by a weighted linear regression analysis of $\ln(I_{obs}-I_0)$ *vs.* time [14].

IR spectra were measured as Nujol mulls or KBr pellets on a *Perkin-Elmer-577* spectrometer, a *Bruker-IFS-113v,* or a *Mattson Alpha Centauri* FT-IR spectrometer. Raman spectra were recorded on a *Spex-Ramalog-4* spectrometer (514.5-nm excitation by means of a *Spectra-Physics-164* Ar-laser). Vibrational data were used to assign vibronic transitions in the luminescence spectra.

Results and Discussion. – The high-resolution $^5D_0 \leftarrow ^7F_0$ excitation spectrum is displayed in *Fig. 1,* and the energies of the $^5D_0$ levels, relative to the $^7F_0$ ground states, are listed in *Table 1.* At room temperature, the spectrum displays three broad bands (fwhh: 10 cm^{-1}). The low-temperature spectrum is more complex; in addition to the expected bathochromic shift and line-narrowing (fwhh: 3–3.5 cm^{-1}), two bands split into two (I) and three (II) components, respectively. Excitation spectra recorded with other analyzing wavelengths did not reveal other components.

To assign the various $^5D_0 \leftarrow ^7F_0$ transitions to specific chemical species, we have selectively excited the Eu(III) ions to their $^5D_0$ levels with wavelengths corresponding to the maxima of bands P, Ia, and IIc. The resulting luminescence spectra are shown in *Fig. 2,* along with the spectrum obtained by exciting simultaneously all the Eu(III) ions to their $^5L_6$ level. Spectrum P is clearly different from the other ones. Its assignment to a pentakis(nitrato) anion with low symmetry (C_2 or lower) is straightforward. The spectrum is indeed dominated by an intense $^5D_0 \rightarrow ^7F_2$ transition, as has been observed for other $[Eu(NO_3)_5]^{2-}$ anions [11] *(cf. Table 2).* Moreover, the energy of the $^5D_0 \leftarrow ^7F_0$ transition is a function of the interelectronic repulsion parameter of the ion, and changes can be thought of as arising from a nephelauxetic effect [16]. Therefore, the greater the negative charge on the ligands, the lower the $^5D_0 \leftarrow ^7F_0$ transition energy. Using the approximate relationship published by *Albin* and *Horrocks* [17], the sum of the formal charges of the ligands bound to the species generating spectrum P is found to be −5.2. The energy of 37 out of 49 ^7F_J sublevels could be calculated from the luminescence spectrum. The crystal-

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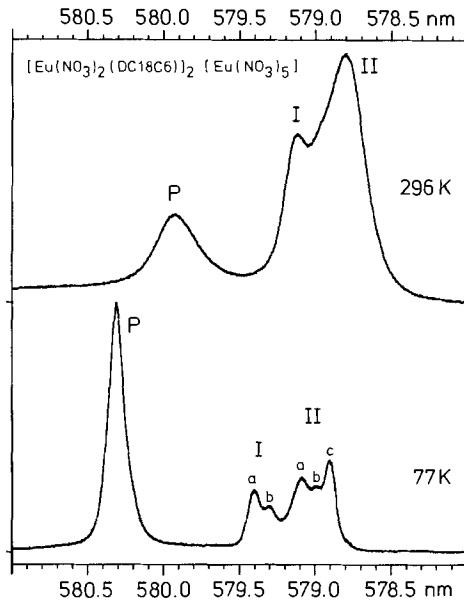[3])   Systematic name: *2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]hexacosane.*

Fig. 1. *Excitation spectrum of [Eu(NO₃)₂(DC18C6)]₂[Eu(NO₃)₅] at 77 and 296 K.* Analyzing wavelength: 613 nm (band-pass: 0.5 nm).

Table 1. *Energies [cm⁻¹] of the $^5D_0$ Levels in [Eu(NO₃)₂(DC18C6)]₂[Eu(NO₃)₅] as Determined from Excitation Spectra at 296 K (λ_{anal} = 616 nm) and 77 K (λ_{anal} = 613 nm)*

T [K]	Component[a])				
	P		I		II
296	17244		17268		17274 (sh)
					17277
77	17232	a	17259	a	17268
		b	17262	b	17271
				c	17274

[a])   For the labels, *cf. Fig. 1.*

Table 2. *Relative Integrated and Corrected Intensities (±10 %) of the $^5D_0 \rightarrow {}^7F_J$ Transitions in the Conventionally and Laser-selectivity Excited Luminescence Spectra of [Eu(NO₃)₂(DC18C6)]₂[Eu(NO₃)₅] at 77 K.* Intensities are normalized with respect to the $^5D_0 \rightarrow {}^7F_1$ transition [15].

J	Band: [a])	P	[b])	Ia	Ib	IIa	IIb	IIc
	λ_{exc} [nm]: 396.0	580.31	580.46	579.40	579.31	579.10	579.00	578.90
0[c])	0.01		0.03[d])					
1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
2	5.6	11.3	8.8	3.5	2.6	2.4	2.4	2.3
3	0.04	0.07	0.07	0.1	0.05	0.06	0.07	0.07
4	2.3	1.7	0.8	4.2	2.2	2.5	2.4	2.5
5		0.1	0.03	0.2				0.1
6		0.4	0.04	1.9				0.6

[a])   Excitation of all Eu(III) ions to their $^5L_6$ level.
[b])   For (Phe₄As)₂[Eu(NO₃)₅]; data from [11].
[c])   The intensity of the $^5D_0 \rightarrow {}^7F_0$ transition cannot be determined under selective excitation to $^5D_0$.
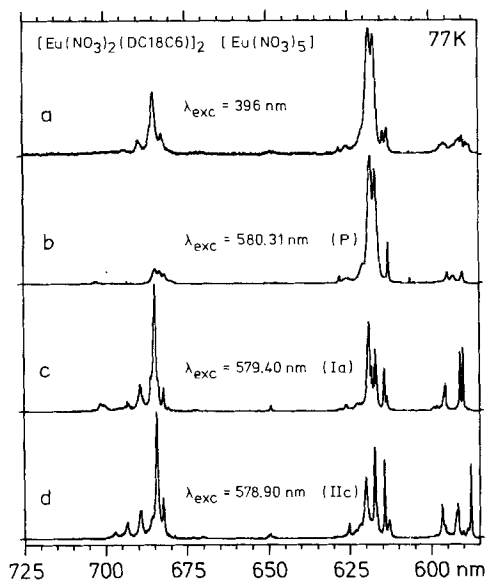[d])   Under excitation to the $^5L_6$ level (395 nm).

Fig. 2. *Luminescence spectra of [Eu(NO$_3$)$_2$(DC18C6)]$_2$[Eu(NO$_3$)$_5$] at 77 K. a) λ_{exc} = 396 nm (band-pass 10 nm),* analyzing band-pass 0.2 nm; *b)–d) selective laser-excitations (band-pass 0.03 nm), analyzing band-pass 0.05 nm.* The vertical scales are not directly comparable.

field splittings are compared in *Fig. 3* with those obtained for the Phe$_4$As$^+$ salt [11]. The similarity in both the pattern and the total span of the splittings is striking, especially for J = 1–4 (data for the very weak $^5D_0 \rightarrow {}^7F_{5,6}$ transitions are difficult to measure). In addition, the barycenters of the ^7F_J levels are also quite similar. This points to a pentakis(nitrato) anion in the DC18C6 complex having a structure close to that in the Phe$_4$As$^+$ salt, a conclusion supported by the crystal-structure determination [1]. The proportionally small crystal-field effect, *e.g.* the splitting of the $^7F_2$ manifold, is attributable to the regular packing of the nitrates around the Eu(III) ion: with one exception (2.37 Å), all the Eu–O distances lie in the range 2.43–2.51 Å.

   The luminescence spectra labelled Ia and IIc in *Fig. 2* differ from spectrum P in that the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition is considerably smaller *(cf. Table 2)*. The sum of the ligand charges q calculated from the energy of the $^5D_0 \leftarrow {}^7F_0$ transition *(Table 1)* is *ca.* −1 for both species. A more precise determination is not possible, since the relationship between q and $\tilde{\nu}(^5D_0 \leftarrow {}^7F_0)$ has a very flat slope when $\tilde{\nu}$ becomes larger than 17 260 (77 K) or 17 270 (296 K) cm^{-1}. The two spectra arise from the complex cations [Eu(NO$_3$)$_2$(DC18C6)]$^+$ and, besides some overall similarities, they display different intensity and splitting patterns, especially in the region of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions. A closer scrutiny of these spectra reveals that in addition to the (2J + 1) components expected for low-symmetry species, some transitions exhibit small additional lines which cannot be assigned as arising from [Eu(NO$_3$)$_5$]$^{2-}$ anions excited through energy transfer. The spectra, therefore, do not correspond to the luminescence of Eu(III) ions lying in a single crystallographic site. To clarify this, we have recorded a series of emission spectra under various excitation wavelengths scanning the Ia–IIc region of the $^5D_0 \leftarrow {}^7F_0$

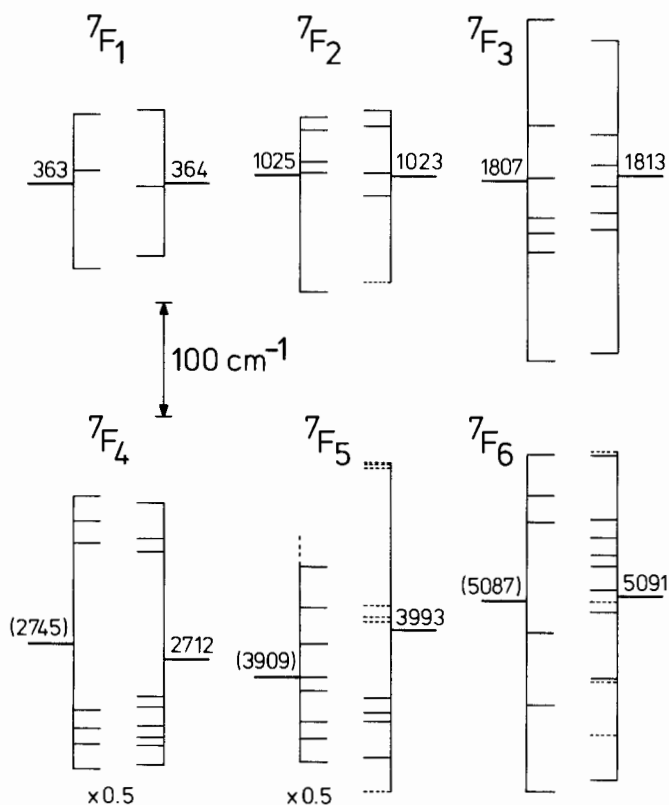Fig. 3. *Crystal-field splittings* [cm^{-1}] *in* [Eu(NO$_3$)$_5$]$^{2-}$ *anions, obtained from luminescence spectra at 77 K. Left: DC18C6 complex, right: Ph$_4$As$^+$ salt, dotted lines represent calculated levels* [11]. *When all the sublevels could not be identified, the barycenters of the* ^{7}F$_J$ *levels are given in parentheses. Note the change in the vertical scale for* ^{7}F$_4$ *and* ^{7}F$_5$.

transition. Each spectrum is comprised of several groups of narrow bands. The barycenter of these groups is shifted, when the exciting wavelength is varied and, more important, the relative intensity of the bands changes dramatically: some components have a small intensity in one spectrum, a more intense one in the next, and then disappear from the other spectra. The situation is schematically represented in *Fig. 4* for the ^{5}D$_0$→^{7}F$_1$ transition. A detailed analysis of all the recorded spectra, taking into account the components arising from the simultaneous excitation of other moieties consecutive to the overlap in the ^{5}D$_0$←^{7}F$_0$ excitation functions, allowed us to classify them into three categories. The first pertains to spectra Ia and Ib which are substantially different from each other, and for which specific ^{7}F$_J$ sublevels could be identified for J = 1–4. The second contains spectra IIa and IIc which display two particular features: *i*) their overall aspect is similar as can be seen from *Fig. 5* and from the relative intensity data gathered in *Table 2*; *ii*) their ^{5}D$_0$→^{7}F$_1$ transition is comprised of 5–6 main components indicating that each spectrum is a mixture of spectra generated by at least two slightly unequivalent chemical species. A similar tendency prevails for the ^{5}D$_0$→^{7}F$_2$ transition (*cf.* the energy sublevels
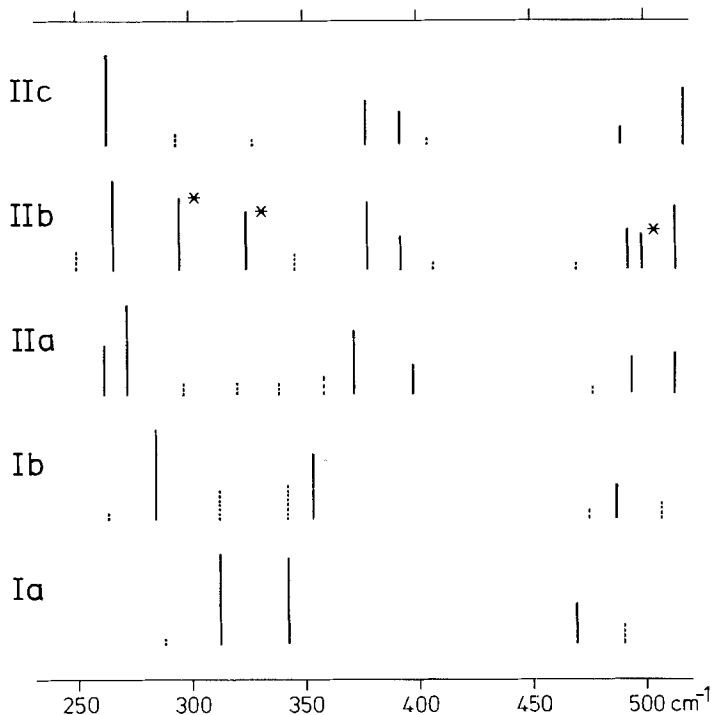
Fig. 4. *Schematic representation of observed* ^7F_J *sublevels at 77 K for the* [Eu(NO₃)₂(DC18C6)]⁺ *cations excited with various wavelengths* (labels: cf. Fig. 1). Each spectrum is normalized with respect to its more intense component. The origin of the energy scale is the corresponding $^7F_0$ level. Dotted lines represent *i)* components arising from another species excited either through energy transfer or because their excitation functions overlap, or *ii)* weak unassigned shoulders. Stars denote the transitions assigned to one of the species generating spectrum IIb (see text). Vibronic transitions are not shown.

listed in *Table 3*[4])). The last category is represented by spectrum IIb which is a mixture of the two other types of spectra: three bands denoted by stars in *Fig. 4* arise from a species similar to those associated with spectra Ia and Ib, while the other components are similar both in shape and positions to those found in spectra IIa and IIc. The assignments made in *Fig. 4* have been checked by means of excitation spectra recorded with a very narrow analyzing band-pass.

Interpreting these experimental facts requires an examination of the crystal structure determination performed at room temperature [1]. Two crystallographically independent [Eu(NO₃)₂(DC18C6)]⁺ cations were found, but their local structures are very similar. On average, these two cations may be considered as chemically equivalent, since most differences in bond lengths and bond angles fall within experimental errors. The only significant difference lies in the temperature factors: half of the atoms of the DC18C6 ligand around Eu(2) have unusually large thermal ellipsoids conferring an appreciable

[4])   The following supplementary material is available from *J.-C. B.* upon request: *a)* a listing of the 345 transitions observed in the emission spectra P, Ia, Ib, IIa, IIb, and IIc; *b)* figures of the $^5D_0 \rightarrow {}^7F_J$ transitions of spectra P, Ia, Ib, IIa, IIb, IIc, and of the spectrum obtained by excitation to the $^5L_6$ level.

Table 3. *Energy of the ^7F_J Sublevels ($J = 0$–4, cm^{-1}) of the Eu(III) Ions in [Eu(NO$_3$)$_2$(DC18C6)]$_2$[Eu(NO$_3$)$_5$], as Identified from Luminescence Spectra at 77 K. Labels: cf. Fig. 1.*

| Level	P	Ia	Ib	IIc
$^7F_0$	0	0	0	0
$^7F_1$	288	312	284	264
	375	337	354	378, 393
	425	469	487	490, 518
$^7F_2$	921	982	961	955, 963, 972
	1026	1054	983	999
	1036	1083	1055	1067, 1077
	1064	1103	1063	1138
	1076	1112	1121	1150
$^7F_3$	1662	1800	1807	1842
	1759	1826	1830	1861
	1776	1857	1856	1863
	1790	1904	1903	1880
	1824	1945	1954	1892
	1871	1987	1995	1908
	1965	2041	2019	1953
$^7F_4$	2526	2571	2573	2624
	2571	2604	2601	2656
	2597	2639	2650	2665
	2629	2658	2670	2669
	2924	2688	2688	2699
	2963	2755	2759	2773
	3007	2831	2853	2779
		2979	2943	2861
		3010	2984	
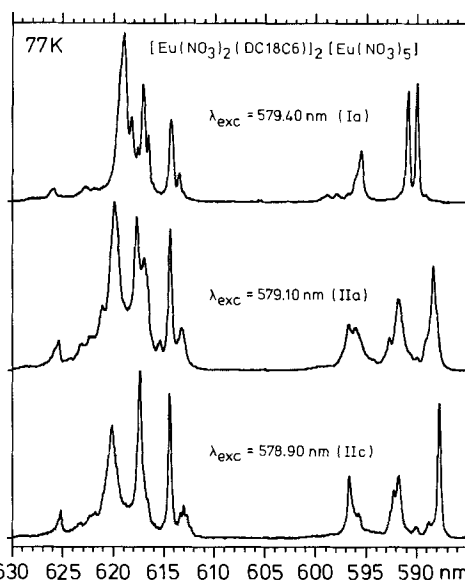
Fig. 5. $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions in the luminescence spectra of [Eu(NO$_3$)$_2$(DC18C6)]$^+$ cations at 77 K obtained under various selective excitations (labels: cf. Fig. 1). Analyzing band-pass: 0.05 nm.

fluxionality to the $-C_6H_{10}(OCH_2CH_2)_2-$ moiety. The luminescence spectra have been recorded at 77 K, since at this temperature the intensity of the vibronic transitions is smaller and the electronic emission bands get sharper. Upon cooling, the thermal motions of the complex molecules are restricted, and individual $[Eu(NO_3)_2(DC18C6)]^+$ cations adopt conformations close to those corresponding to minima in the potential energy curve; this leads to the maxima observed in the excitation spectrum of *Fig. 1*. Since the large thermal motions of DC18C6 bound to Eu(2) involve the O-atoms O(5) and O(6), we assign spectra Ia, Ib, and the components denoted by stars in spectrum IIb to energetically favourable conformations of $[Eu(2)(NO_3)_2(DC18C6)]^+$. The position of the O-atoms may differ from one conformation to the other, inducing geometrical changes in the EuO_{10} coordination polyhedron, hence the differences observed in the crystal field splittings *(cf. Fig. 4)*. Spectra IIa, IIc, and the other part of spectrum IIb are less differentiated, and they probably arise from $[Eu(1)(NO_3)_2(DC18C6)]^+$ cations with slightly different conformations, due to the fluxionality of the ethylene bridges.

Although this assignment cannot be formally proved, it is supported by the relative transition probabilities calculated from the band area of the $^5D_0 \rightarrow ^7F_1$ transition. The oscillator strength of this magnetic dipole transition is indeed independent of the Eu(III) environment, and its band area is, therefore, directly proportional to the number of Eu(III) ions in a given chemical environment [15]. The contribution of $[Eu(NO_3)_5]^{2-}$ to the $^5D_0 \rightarrow ^7F_1$ transition in the spectrum obtained under excitation to the $^5L_6$ level is 30%, a value close to the expected one (33%). Intensity comparisons between the laser-excited spectra of the complex cations gave the following contributions: 20% (Ia, IIc), 12% (IIa), 10% (Ib), and 8% (IIb, each species contributes 4%). Summing up the contributions of Ia, Ib, IIb (one species denoted by stars) on one hand, and IIa, IIb (the other species), IIc on the other hand leads to 34% and 36%, respectively. Accordingly, our assignment corresponds to a relative population of 0.9:1.0:1.1 for the three crystallographically distinct moieties.

It is noteworthy that the overall differences between spectra Ia through IIc are not very large, but can be unraveled because they are magnified by the high resolution and high sensitivity of our experiments. Lifetimes could also be measured selectively for species labelled P, Ia, and IIc. At 77 K, the two complex cations have an identical lifetime, 1.57(5) ms, which prevents further differentiation between the different conformations the ligand may adopt. These lifetimes are almost temperature-independent (1.46(1) ms at 296 K) meaning that a large number of vibrational quanta are involved in the non-radiative process [18]. The lifetime of the $[Eu(NO_3)_5]^{2-}$ anion is shorter (1.09(2) ms) and exhibits an apparent temperature dependence. In fact, the variation observed arises from efficient energy-transfer processes taking place at room temperature so that the lifetimes measured at 296 K are an average of the cation and anion lifetimes.

Conclusion. – This study confirms the extreme sensitivity of the Eu(III) ion as spectroscopic probe. Indeed, a high-resolution analysis of the luminescence spectra generated by an Eu-containing material allows one to recognize the presence of molecules possessing different conformations. At present, this solid-state conformational analysis remains essentially descriptive and qualitative. However, it provides a welcome complement to diffraction studies which yield only an average description of the unit cell content.

REFERENCES

[1] F. Nicolò, D. Plancherel, J.-C. G. Bünzli, G. Chapuis, *Helv. Chim. Acta* **1987,** *70,* 1798.

[2] G. Mathis, J.-M. Lehn, Fr. Pat. 2 570 703, 1986.

[3] J. C. Wright, in 'Modern Fluorescence Spectroscopy', Ed. E. L. Wehry, Plenum Press, New York, 1982, Vol. 4, Chapt. 3.

[4] C. A. Morrison, R. P. Leavitt, in 'Handbook on the Physics and Chemistry of Rare Earths', Eds. K. A. Gschneidner, Jr. and L. Eyring, North-Holland Publ. Co., Amsterdam, 1982, Vol. 5, Chapt. 46.

[5] J. B. Gruber, R. P. Leavitt, C. A. Morrison, N. C. Chang, *J. Chem. Phys.* **1985,** *82,* 5373.

[6] M. J. Weber, in 'Topics in Applied Physics', Eds. W. M. Yen and P. M. Selzer, Springer-Verlag, Berlin, 1981, Vol. 49, Chapt. 6.

[7] J.-C. G. Bünzli, *Inorg. Chim. Acta* **1987,** *139,* in press.

[8] F. S. Richardson, *Chem. Rev.* **1982,** *82,* 541.

[9] J.-C. G. Bünzli, G.-O. Pradervand, *J. Chem. Phys.* **1986,** *85,* 2489.

[10] J.-C. G. Bünzli, G. A. Leonard, D. Plancherel, G. Chapuis, *Helv. Chim. Acta* **1986,** *69,* 288.

[11] J.-C. G. Bünzli, B. Klein, G.-O. Pradervand, P. Porcher, *Inorg. Chem.* **1983,** *22,* 3763.

[12] J.-C. G. Bünzli, B. Klein, G. Chapuis, K. J. Schenk, *Inorg. Chem.* **1982,** *21,* 808.

[13] S. W. Provencher, *Biophys. J.* **1976,** *16,* 37; *J. Chem. Phys.* **1976,** *64,* 2772.

[14] K. J. Johnson, 'Numerical Methods in Chemistry', Marcel Dekker, New York, 1980.

[15] P. Porcher, P. Caro, *J. Luminesc.* **1980,** *21,* 207.

[16] C. K. Jørgensen, *Prog. Inorg. Chem.* **1962,** *4,* 73; F. Durville, G. Boulon, R. Reisfeld, H. Mack, C. K. Jørgensen, *Chem. Phys. Lett.* **1983,** *102,* 393.

[17] M. Albin, W. DeW. Horrocks, Jr., *Inorg. Chem.* **1985,** *24,* 895.

[18] F. Auzel, *Phys. Rev. B: Sol. State* **1976,** *13,* 2809.